



## Research paper

Cooperative luminescence mediated near infrared photocatalysis of  $\text{CaF}_2:\text{Yb}@\text{BiVO}_4$  composites

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## ABSTRACT

It is a challenge to develop efficient photocatalyst that can be activated by photons with long wavelength. In our previous work, a near infrared (NIR) driven photocatalyst (e.g.,  $\text{NaYF}_4:\text{Yb,Tm}@\text{TiO}_2$ ) was designed, for which, however, a two-step energy transfer was involved for photocatalysis so that the ultimate photocatalytic capability is low. In this work, we designed and prepared a new type of NIR photocatalyst composed of cooperative luminescence agent  $\text{CaF}_2:\text{Yb}$  and semiconductor  $\text{BiVO}_4$ , in which a one-step energy transfer occurs to realize NIR photocatalysis. Steady-state and dynamic fluorescence spectroscopy analysis revealed that cooperative energy transfer of a  $\text{Yb}^{3+}$ -dimer to  $\text{BiVO}_4$  leads to the indirect excitation of semiconductor  $\text{BiVO}_4$  by NIR light. The degradation of methylene blue (MB) compound by  $\text{CaF}_2:1\%\text{Yb}^{3+}@\text{BiVO}_4$  particles upon NIR radiation and its corresponding controlled experiments demonstrated the NIR light responsive photocatalytic capability. It is noteworthy that nearly 80% degradation ratio of MB was achieved with 7 h of NIR light irradiation, indicating a relatively high photocatalytic activity, compared with that of our previously reported system  $\text{NaYF}_4:\text{Yb,Tm}@\text{TiO}_2$ , for which ~65% of degradation ratio of MB was obtained within 14 h of NIR irradiation. Recycling experiments of photocatalysis indicate that our present  $\text{CaF}_2:\text{Yb}@\text{BiVO}_4$  composite has good photochemical stability in spite of a long time of NIR irradiation.

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## 1. Introduction

Photocatalysis is an economical and environmentally friendly technique that can be applied in environmental remediation, solar energy conversion, and organic photosynthesis [1–5]. Since Fujishima and Honda discovered the photocatalytic water-splitting on crystalline  $\text{TiO}_2$  electrodes for hydrogen production in 1972 [6], research interests in  $\text{TiO}_2$  photocatalysis have grown significantly owing to its strong oxidizing power under ultraviolet (UV) light, extraordinary chemical stability, as well as environmental friendly and biocompatible features [7–15]. However,  $\text{TiO}_2$  with crystalline anatase phase has a bandgap of ~3.2 eV, and mainly absorbs UV light [16], which accounts for only about 5% of the incoming solar energy. Therefore, visible and infrared photons with energy lower than the bandgap energy of  $\text{TiO}_2$ , which occupies more than 90% of the solar energy, cannot be harvested for photocatalysis [17,18].

To address this problem, much effort has been devoted to extending the absorption of  $\text{TiO}_2$  to the long wavelength region for efficient use of solar energy. To reach this goal, several strategies have been proposed by adjusting the bandgap toward visible light

energies through the introduction of noble metals, cationic substitutions, and anionic doping [19–27]. Although the absorption of  $\text{TiO}_2$  by these modification methods could be adjusted to the visible region, the overall catalytic capability was found to decrease due to an increased recombination of photogenerated electrons and holes [28–30]. Therefore, it is still a challenge to find an appropriate way to extend the absorption of  $\text{TiO}_2$  to visible and NIR region.

Recently, our group has first reported the activation of broadband semiconductor by NIR phonons for photocatalysis via combining upconverting luminescence agent  $\text{YF}_3:\text{Yb,Tm}$  and semiconductor  $\text{TiO}_2$  to construct a core-shell structure, in which  $\text{YF}_3:\text{Yb,Tm}$  acts as a mediate for converting NIR to UV light via a multiphoton upconversion process [31]. In the subsequent work, we investigated the energy transfer process between upconverting luminescent agent and semiconductor by steady-state and dynamic fluorescence spectroscopy, and revealed that the fluorescence resonant energy transfer dominated for NIR photocatalysis in such a core-shell structure [32]. Later, our idea of activating broadband semiconductor by NIR photons has been transplanted and applied in the areas of  $\text{H}_2$  production via water splitting [33,34], photovoltaic device [35,36] and photodynamic therapy [37–39] by other research groups.

Indeed, there exists a two-step energy transfer for realizing NIR-responsive photocatalysis in our previously designed catalytic

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material, i.e.,  $\text{Yb}^{3+}$ – $\text{Tm}^{3+}$  energy transfer first, and then  $\text{Tm}^{3+}$ – $\text{TiO}_2$  energy transfer. As we have known, multiple-step energy transfer would increase the loss of photo energy significantly and reduce the ultimate efficiency of energy transfer to  $\text{TiO}_2$  largely, resulting in a low photo quantum yield for exciting  $\text{TiO}_2$ . Therefore, it seems a promising strategy to reduce the energy transfer procedures for improving the photo quantum efficiency of exciting  $\text{TiO}_2$ , and thus increasing the NIR-light responsive photocatalytic activities.

Cooperative luminescence refers to a process by which a pair of ions emits one photon by simultaneous depopulation from their excited states [40–42]. The cooperative luminescence of a pair of excited  $\text{Yb}^{3+}$ -ions was first observed in 1970 [40]. Very recently, our group has reported the cooperative luminescence involving three neighboring  $\text{Yb}^{3+}$ -ions in  $\text{CaF}_2$  host, in which the UV emission is observed under NIR excitation [43]. Clearly, the cooperative luminescence shows a novel upconversion luminescent mechanism, for which the energy transfer process is not involved. In this work, guided by this special upconversion luminescence mechanism, we designed a new type of NIR-activatable photocatalytic material by combining a typical cooperative luminescence agent  $\text{CaF}_2:\text{Yb}$  and a well-known semiconductor  $\text{BiVO}_4$ , in which NIR light photocatalysis was achieved via a one-step energy transfer process. Due to the reduction of energy transfer procedures for our present catalytic material in this work, the photocatalytic activity was improved remarkably, compared with that of our previously reported NIR-responsive catalytic system (e.g.,  $\text{NaF}_4:\text{Yb}$ ,  $\text{Tm@TiO}_2$ ) [32].

## 2. Experimental

### 2.1. Preparation of $\text{CaF}_2:1\%\text{Yb}^{3+}$

The powder sample of  $\text{CaF}_2:1\%\text{Yb}^{3+}$  was prepared using a high temperature solid-state reaction method. The raw materials  $\text{CaF}_2$  and  $\text{YbF}_3$  were thoroughly mixed by grinding together, and then heated up to  $1400^\circ\text{C}$  for 2 h in an argon atmosphere and quenched to room temperature.

### 2.2. Preparation of $\text{CaF}_2:1\%\text{Yb@BiVO}_4$

The  $\text{CaF}_2:\text{Yb@BiVO}_4$  composite was prepared by a conventional co-precipitation method. In a typical process, 0.5 mmol as-prepared  $\text{CaF}_2:1\%\text{Yb}$  and 0.1 mmol  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  were dispersed into 10 mL  $\text{HNO}_3$  solution (2 M), and 0.1 mmol  $\text{NH}_4\text{VO}_3$  was dispersed into 10 mL  $\text{NH}_3 \cdot \text{H}_2\text{O}$  solution (2 M) under violent stirring. Then, the solution containing  $\text{Bi}(\text{NO}_3)_3$  and  $\text{CaF}_2:1\%\text{Yb}$  was added to the  $\text{NH}_4\text{VO}_3$  solution slowly under violent stirring. After stirring for 3 h, the pH of the mixed solution was adjusted to 7 using  $\text{NH}_3 \cdot \text{H}_2\text{O}$  solution and then the mixed solution was kept stirring for another 12 h to get a homogeneous solution. The obtained solution was transferred into a 20 mL stainless autoclave with a Teflon liner and then the stainless autoclave was maintained at  $180^\circ\text{C}$  for 24 h. After cooling down to room temperature naturally, the obtained products were washed with MilliQ water and ethanol for three times, respectively. The obtained samples were dried in  $70^\circ\text{C}$  for 24 h in a drying oven. For comparison, we prepared the  $\text{CaF}_2:\text{Yb@BiVO}_4$  composites with different  $\text{CaF}_2:\text{Yb}$ -to- $\text{BiVO}_4$  molar ratios (10:0.5, 10:1, 10:2, 10:3, 10:4, respectively).

### 2.3. Characterization

The purity and phase structure of the resulting products were analyzed with a Model Rigaku Ru-200b X-ray powder diffractometer (XRD) using a nickel-filtered Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the 2-Theta ranging from  $10^\circ$  to  $70^\circ$ . Field-emission scanning electron microscopy (SEM) images were recorded using a JEOL

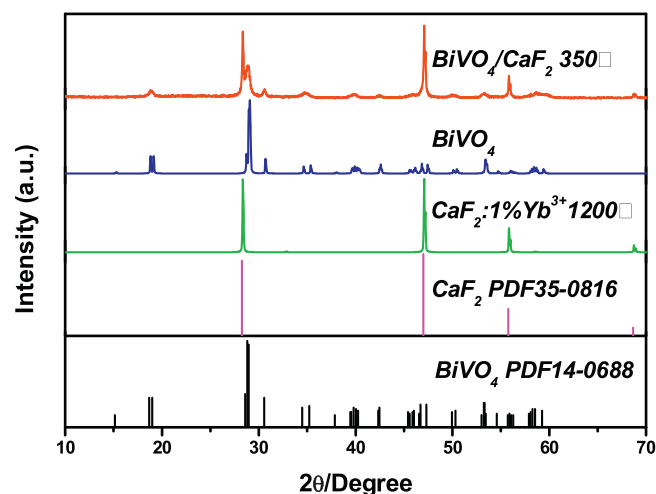


Fig. 1. XRD patterns of  $\text{CaF}_2:\text{Yb}$  with and without  $\text{BiVO}_4$  deposition. Standard XRD patterns of JCPDS 35-0816 ( $\text{CaF}_2$ ) and 14-0688 ( $\text{BiVO}_4$ ) are also shown.

JSM-7500F microscope operating at 5 kV at a working distance of 2–3 mm. For the SEM observations, samples were prepared without any carbon coating simply by depositing some powder onto a silicon slice. The UV-vis-NIR diffuse reflectance spectrum was recorded with a Shimadzu UV-3600 in the wavelength ranged of 200–1000 nm, using  $\text{BaSO}_4$  for background scanning. Raman spectra were recorded at room temperature using a LabRAM HR evolution Raman spectrometer (Horiba Scientific) in the back-scattering geometry with a 532 nm semiconductor as an excitation source. Power-adjustable continuous wave laser diodes (978 nm, 10 W, BWT Beijing Ltd, Beijing, China) were employed as the pump sources for spectral analysis. The luminescence spectra were recorded with an 1-m monochromator (SPEX 1000 M, model: 232/488MSD; HORIBA Jobin Yvon Inc., Edison, NJ, USA) equipped with a 1800 lines  $\text{mm}^{-1}$  for visible fluorescence grating. A digital oscilloscope (DPO4104B, bandwidth 1 GHz, sampling rate  $5 \text{ GSs}^{-1}$ ; Tektronix, Shanghai, China), a power-adjustable continuous wave laser diode (CW978 nm, 10 W), and a chopper were used to record decay curves.

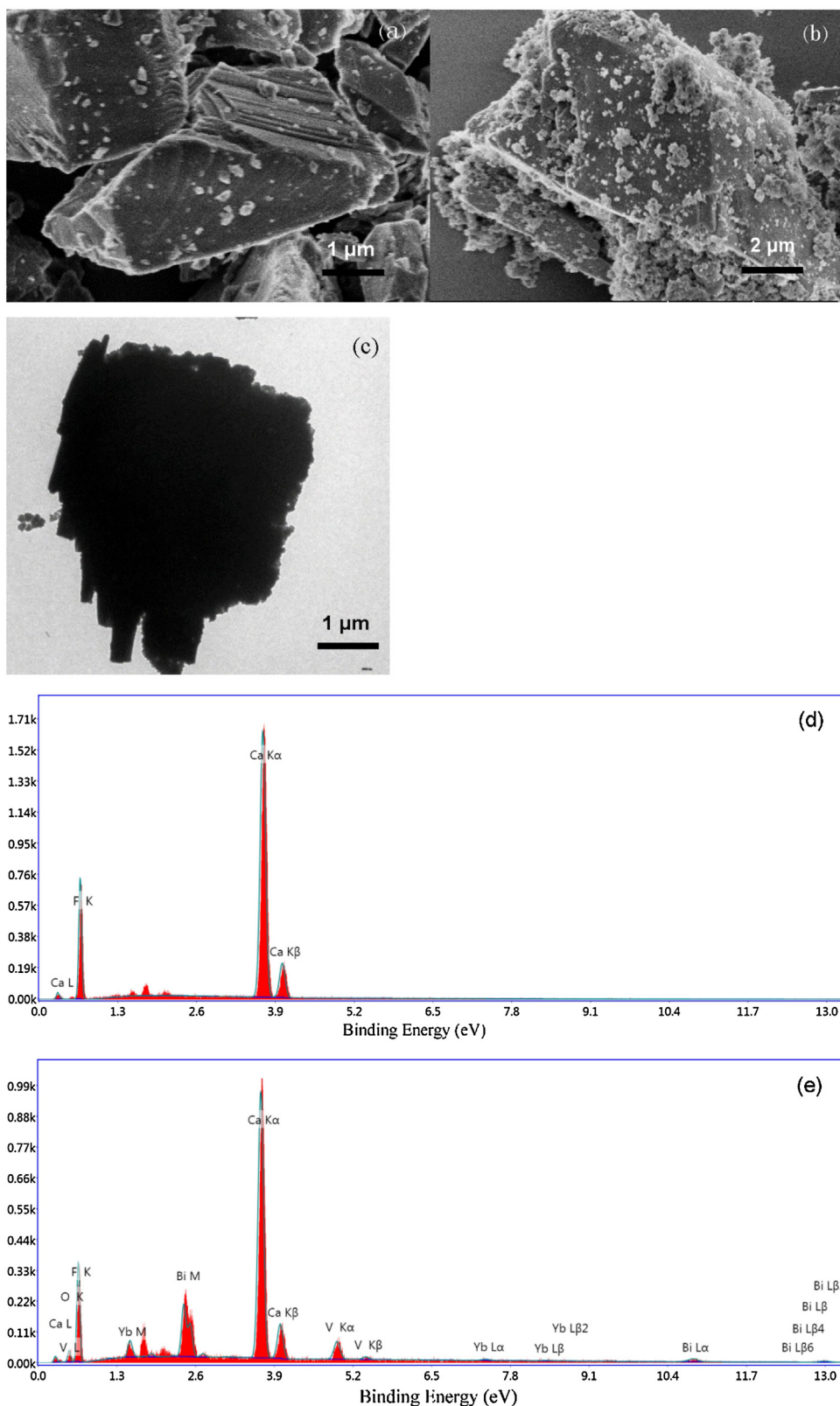
### 2.4. Photocatalytic experiments

The photocatalysis was performed with NIR irradiation in the presence of photocatalyst using methyl blue (MB) as a model pollutant. The degradation of MB was evaluated by measuring its optical absorption using a Shimadzu UV-3600 spectrophotometer. In a typical experiment, 0.5 mg of  $\text{CaF}_2:\text{Yb@BiVO}_4$  particles was dispersed into a quartz cuvette containing 0.5 mL of MB aqueous solution ( $15 \text{ mg L}^{-1}$ ), and then kept in the dark prior to irradiation for establishing adsorption-desorption equilibrium of MB on the surface of  $\text{CaF}_2:\text{Yb@BiVO}_4$  particles before irradiation. A diode laser of 980 nm with a power of  $10 \text{ W/cm}^2$  was used as the irradiation source. After irradiation of 980 nm light for a designated time, 0.3 mL of MB aqueous solution was taken out for UV-vis absorbance measurements, and then put back into the quartz corvette. The concentration of MB solution at each time interval was calculated using the calibration curve of the standard solution.

## 3. Results and discussion

### 3.1. Phase and morphological characterization

Fig. 1 shows the XRD pattern of the product obtained via high temperature sintering of  $\text{CaF}_2$  and  $\text{YbF}_3$  mixtures at Ar atmo-



**Fig. 2.** SEM (a, b) and TEM images (c) and EDX spectra (d, e) of  $\text{CaF}_2:\text{Yb}$  and  $\text{CaF}_2:\text{Yb}@\text{BiVO}_4$  composites.

sphere. The position and relative intensity of all diffraction peaks can be readily indexed to cubic  $\text{CaF}_2$  phase, compared with the JCPDS file NO. 35-0816. No impurity was detected, indicating that the as-prepared product was single-phased. The particle size and morphology of Yb-doped  $\text{CaF}_2$  phosphors were investigated

through SEM. Fig. 2(a) presents a typical SEM image of as-prepared  $\text{CaF}_2:1\%\text{Yb}$  phosphors, in which large particles with the size of 5–10  $\mu\text{m}$  are observed.

Upon the addition of  $\text{Bi}(\text{NO}_3)_3$  and  $\text{NH}_4\text{VO}_3$  solutions to  $\text{CaF}_2$  powders at acidic condition, followed by a hydrothermal treatment

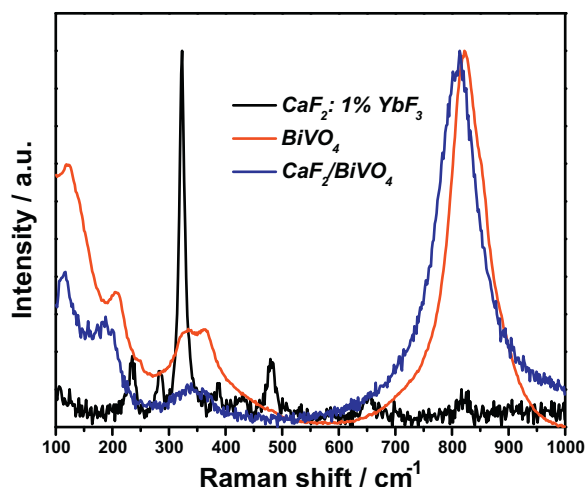


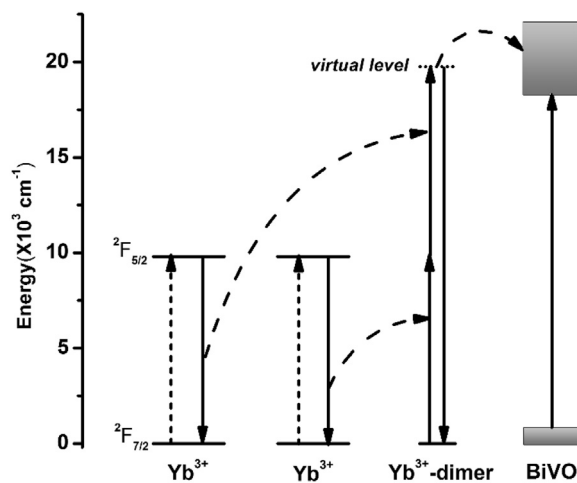
Fig. 3. Raman spectra of  $\text{CaF}_2\text{:Yb}$ ,  $\text{BiVO}_4$  and  $\text{CaF}_2\text{:Yb@BiVO}_4$  composite.

at 160 °C for 24 h, a number of small sized particles were found to deposit on the  $\text{CaF}_2$  particles (Fig. 2b and c). As shown in the XRD pattern (Fig. 1), these nanoparticles are composed of monoclinic phased  $\text{BiVO}_4$  corresponding to the JCPDS file NO. 14-0688, while  $\text{CaF}_2$  still maintains the cubic structure. It is noted that a few neighboring diffraction peaks are merged into a broad peak, indicating a small size of  $\text{BiVO}_4$  particles. The EDX spectrum shown in Fig. 2 reveals that the  $\text{CaF}_2\text{:Yb}$  sample deposited with  $\text{BiVO}_4$  consists of Ca, Yb, F, Bi, V, and O (Fig. 2(e)), corresponding to the composition of  $\text{CaF}_2$  and  $\text{BiVO}_4$ , while the sample composed of  $\text{CaF}_2\text{:Yb}$  alone consists of Ca, F, and Yb (Fig. 2(d)).

Fig. 3 shows the Raman spectra of individual  $\text{CaF}_2\text{:Yb}$  and  $\text{BiVO}_4$ , and  $\text{CaF}_2\text{:Yb@BiVO}_4$  composite. For  $\text{CaF}_2\text{:Yb}$  alone, several peaks located at 235, 284, 324, 385, 482 and 656  $\text{cm}^{-1}$  are observed, which are attributed to the vibration mode of  $\text{CaF}_2$  [44,45]. Upon the deposition of  $\text{BiVO}_4$  nanoparticles onto  $\text{CaF}_2$  particles, additional vibration peaks at 121, 207, 327, 364 and 821  $\text{cm}^{-1}$  appears, which belong to characteristic vibrational modes of  $\text{BiVO}_4$  [46]. Among them, the vibration peak at 821  $\text{cm}^{-1}$  is the strongest, corresponding to the symmetric stretching vibration of vanadate units. It is worth noting that the Raman peaks of  $\text{BiVO}_4$  in the composite is red-shifted, compared with those of  $\text{BiVO}_4$  alone, indicating the formation of  $\text{CaF}_2\text{:Yb@BiVO}_4$  composite. The photoluminescence characterization of resulting product provides further evidence of the successful deposition of  $\text{BiVO}_4$  nanoparticles on the  $\text{CaF}_2$  particles (see below).

### 3.2. Photoluminescence and energy transfer

$\text{CaF}_2\text{:1%Yb}^{3+}$  is a typical cooperative luminescence material. In  $\text{Yb}^{3+}$ -doped  $\text{CaF}_2$  host,  $\text{Yb}^{3+}$  ions substitute for  $\text{Ca}^{2+}$  ions and are situated in nearly tetragonal crystal-field environments. At 1-mol% dopant concentration,  $\text{Yb}^{3+}$  ions doped into  $\text{CaF}_2$  prefer to form the clusters [43]. Under the pumping of a NIR laser, a pair of  $\text{Yb}^{3+}$  ions (a  $\text{Yb}^{3+}$ -dimer) were both excited from  $^2F_{7/2}$  to  $^2F_{5/2}$  level, and then depopulated from excited state  $^2F_{5/2}$  simultaneously to emit a visible photon, which is called as cooperative luminescence (see Scheme 1). Fig. 4 shows the photoluminescence spectrum of  $\text{CaF}_2\text{:1%Yb}^{3+}$  under 980 nm excitation. We can see a broad band ranging from 470 to 570 nm, which originates from the cooperative luminescence of  $\text{Yb}^{3+}$ -dimers. It is found that this broad band is composed of a few sharp emission peaks that are connected with each other. It is well known that the  $^2F_{5/2}$  to  $^2F_{7/2}$  levels of  $\text{Yb}^{3+}$  ions split into three and four Stark components in a tetragonal crystal field, respectively [47]. Therefore, a random combination



Scheme 1. Cooperative luminescence of a  $\text{Yb}^{3+}$ -dimer in  $\text{CaF}_2$  host and cooperative sensitization of  $\text{BiVO}_4$  by a  $\text{Yb}^{3+}$ -dimer.

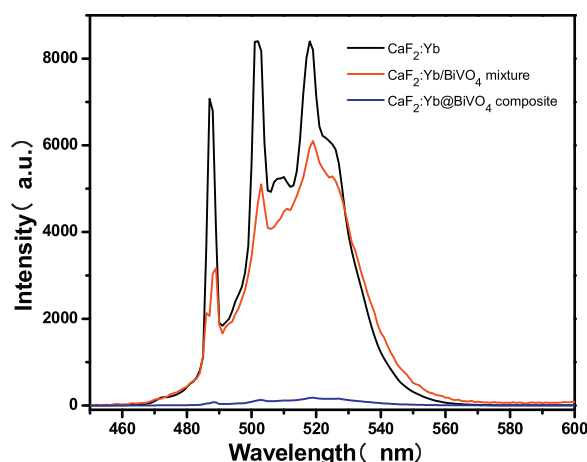


Fig. 4. Photoluminescence (PL) spectra of  $\text{CaF}_2\text{:1%Yb}^{3+}$ , a physical mixture of  $\text{CaF}_2\text{:1%Yb}^{3+}$  and  $\text{BiVO}_4$ ,  $\text{CaF}_2\text{:1%Yb}^{3+}\text{@BiVO}_4$  composite under 980 nm excitation at room temperature.

of two Stark components in cooperative luminescence of a  $\text{Yb}^{3+}$ -dimer forms an emission located at different energies but close to each other [43]. These approaching emission peaks are connected to form a broad band.

After depositing  $\text{BiVO}_4$  nanoparticles onto the surface of  $\text{CaF}_2\text{:Yb}$  particles, the remarkable spectral difference can be observed (Fig. 4). The emission of  $\text{CaF}_2\text{:Yb}$  nearly disappears. For comparison, the physical mixture of  $\text{CaF}_2\text{:Yb}$  and  $\text{BiVO}_4$  was also prepared by mixing both of them via grinding. The emission of  $\text{CaF}_2\text{:Yb}$  shows a slight decrease for the  $\text{CaF}_2\text{:Yb/BiVO}_4$  mixture (Fig. 4).

To ascertain the origin of the above spectral difference, the UV-vis-NIR absorption of  $\text{CaF}_2\text{:Yb@BiVO}_4$  composites was measured and recorded in Fig. 5. In the spectrum, except for the absorption of  $\text{Yb}^{3+}$  around 980 nm (inset), a well-defined absorption band starting at  $\sim 540$  nm was observed, corresponding to the bandgap absorption of semiconductor  $\text{BiVO}_4$  [48]. Therefore we can speculate that the visible photon energy generated via a cooperative luminescence process of  $\text{Yb}^{3+}$ -dimers can be absorbed by semiconductor  $\text{BiVO}_4$  via an energy transfer between them for the sample  $\text{CaF}_2\text{:Yb@BiVO}_4$ . But for the  $\text{CaF}_2\text{:Yb/BiVO}_4$  mixture, the energy transfer between  $\text{CaF}_2\text{:Yb}$  and  $\text{BiVO}_4$  is difficult to take place due to a large distance between them.

Such a conclusion was further supported by the fluorescence dynamic analysis of  $\text{Yb}^{3+}$ . The fluorescence dynamic curves of



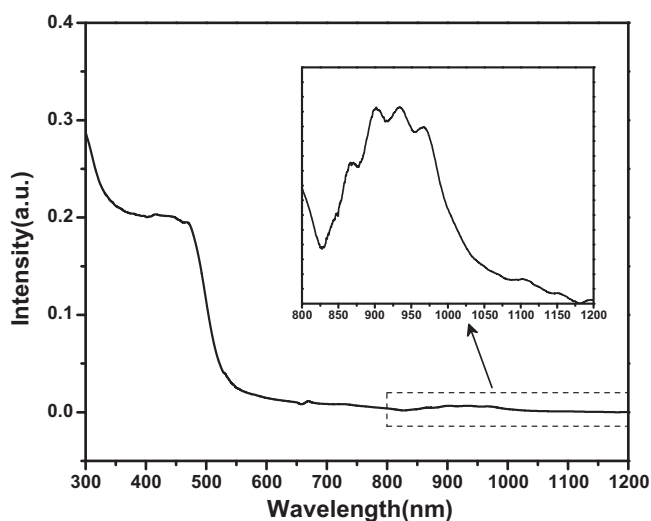


Fig. 5. UV-vis-NIR absorption spectra of  $\text{CaF}_2\text{:Yb@BiVO}_4$  composite.

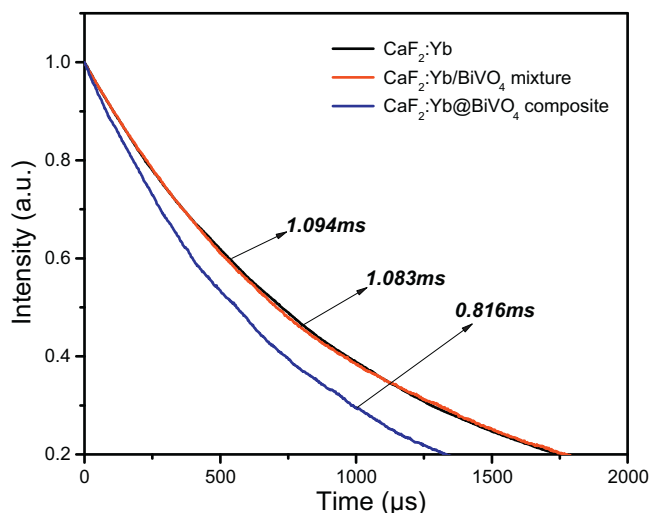


Fig. 6. Luminescence dynamic curves of  $\text{Yb}^{3+}$ -dimers in  $\text{CaF}_2\text{:Yb}$ ,  $\text{CaF}_2\text{:Yb/BiVO}_4$  mixture and  $\text{CaF}_2\text{:Yb@BiVO}_4$  composite under 978 nm excitation.

$\text{Yb}^{3+}$ -dimer emission (521 nm) were recorded under excitation of a 978 nm laser for the samples  $\text{CaF}_2\text{:Yb}$ ,  $\text{CaF}_2\text{:Yb@BiVO}_4$  composite and  $\text{CaF}_2\text{:Yb/BiVO}_4$  mixture, as shown in Fig. 6. For  $\text{CaF}_2\text{:Yb}$  alone, the lifetime of cooperative excited state of a  $\text{Yb}^{3+}$ -dimer is long with  $\sim 1.094$  ms. The long-lived excited state of lanthanide ions ensures an efficient energy transfer to semiconductor. As observed, the decay time of the  $\text{Yb}^{3+}$ -dimer excited level decreased to 0.816 ms in the  $\text{CaF}_2\text{:Yb@BiVO}_4$  composite, while almost no change was observed for the  $\text{CaF}_2\text{:Yb/BiVO}_4$  mixture (1.083 ms), compared with that of  $\text{CaF}_2\text{:Yb}$ . It is reasonable to infer that the energy of the excited state of  $\text{Yb}^{3+}$ -dimer can be transferred directly to semiconductor  $\text{BiVO}_4$  in the  $\text{CaF}_2\text{:Yb@BiVO}_4$  composite, since the cooperative excited energy of a  $\text{Yb}^{3+}$ -dimer in  $\text{CaF}_2$  overlaps well with the bandgap of semiconductor  $\text{BiVO}_4$  (see Scheme 1). Such energy transfer behavior was also observed in our previously reported  $\text{NaYF}_4\text{:Yb,Tm@TiO}_2$  and  $\text{NaYF}_4\text{:Yb,Tm@ZnO}$  systems [32,49].

As we know, the lifetime of an excited state,  $\tau$ , is determined by the radiative transition rate ( $W_R$ ), the nonradiative transition rate ( $W_{NR}$ ), and the energy transfer rate ( $W_{ET}$ ), which can be expressed as  $\tau = 1/(W_R + W_{NR} + W_{ET})$  [49,50]. The presence of  $\text{BiVO}_4$  deposited on the  $\text{CaF}_2\text{:Yb}$  particle surface creates nonradiative energy trans-

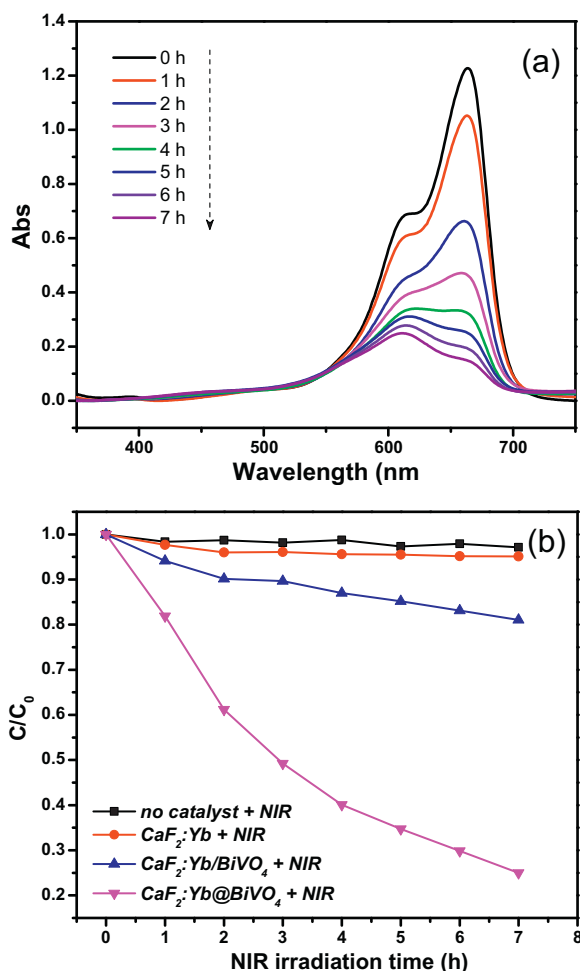
fer channels from the cooperative excited state of a  $\text{Yb}^{3+}$ -dimer to  $\text{BiVO}_4$ . Such additional energy transfer process obviously accelerates the relaxation of the excited states of  $\text{Yb}^{3+}$ -dimers, resulting in the increase of overall transition rates and thus the reduction of fluorescence lifetime. The shortening of fluorescence lifetime of  $\text{Yb}^{3+}$ -dimers in the  $\text{CaF}_2\text{:Yb@BiVO}_4$  composite indicates that the energy migration between  $\text{CaF}_2\text{:Yb}$  and  $\text{BiVO}_4$  is dominated by a fluorescence resonance energy transfer (FRET) process, rather than by a radiation-reabsorption process, because the fluorescence lifetime of the donor is unchanged in the latter process. Therefore, the cooperative energy of the excited states of a  $\text{Yb}^{3+}$ -dimer is transferred directly to semiconductor  $\text{BiVO}_4$ , leading to a significant decrease of the emission of  $\text{Yb}^{3+}$ -dimers (Fig. 4). For the  $\text{CaF}_2\text{:Yb/BiVO}_4$  mixture, the lifetime of excited state of  $\text{Yb}^{3+}$ -dimer is almost unchanged, compared with that for the sample  $\text{CaF}_2\text{:Yb}$ , indicating a radiation-reabsorption process for the energy transfer from  $\text{CaF}_2\text{:Yb}$  to  $\text{BiVO}_4$ . Moreover, the energy transfer is inefficient due to a relatively large distance between  $\text{CaF}_2\text{:Yb}$  and  $\text{BiVO}_4$  in the  $\text{CaF}_2\text{:Yb/BiVO}_4$  mixture, corresponding to a slight decrease of  $\text{Yb}^{3+}$ -dimer emission (Fig. 4). Indeed, the difference of the energy transfer mechanism affects the photocatalytic activity of  $\text{BiVO}_4$  significantly, which will be discussed in the section below.

### 3.3. Photocatalytic activity

As discussed earlier, the n-type semiconductor  $\text{BiVO}_4$  is activated mainly by the energy transfer from excited  $\text{Yb}^{3+}$ -dimers via a FRET process in the  $\text{CaF}_2\text{:Yb@BiVO}_4$  composite. Thus, the electrons and holes are generated in the conduction band (CB) and the valence band (VB), respectively, and then these electron-hole pairs migrate from the inner region to the surfaces to take part in surface reactions. The separated electrons and holes arriving on the surface react with  $\text{O}_2$  and  $\text{H}_2\text{O}$  to generate  $\cdot\text{OH}$  and  $\text{O}_2^{\cdot-}$ . These reactive oxygen species with strong oxidation ability can oxidize pollutant molecules and perform photocatalysis [51–54].

Methylene blue (MB) compound as a model pollutant was used to investigate the photocatalytic activity of the  $\text{CaF}_2\text{:Yb@BiVO}_4$  composite under NIR irradiation of 980 nm. 0.5 mg of  $\text{CaF}_2\text{:Yb@BiVO}_4$  particles was dispersed into a quartz cuvette containing 0.5 mL of MB aqueous solution ( $15 \text{ mg L}^{-1}$ ). For comparing the photocatalytic activity, the concentrations of the catalyst and pollutant and NIR irradiation power used in this work are the same as those in our previous work [32]. Prior to the photocatalysis experiment, the dark reaction of MB in the presence of catalysts was conducted to establish adsorption/desorption equilibrium of MB on the surfaces of  $\text{CaF}_2\text{:Yb@BiVO}_4$  particles.

Fig. 7(a) shows the absorbance spectra of MB catalyzed by the  $\text{CaF}_2\text{:Yb@BiVO}_4$  particles under 980 nm irradiation as a function of irradiation time. The absorbance band around 664 nm is characteristic of MB. We can see that the absorbance of MB decreases gradually with an increase of irradiation time, indicating the degradation of MB upon NIR irradiation. The photocatalytic activity of  $\text{CaF}_2\text{:Yb@BiVO}_4$  can be evaluated through the concentration of MB after NIR irradiation relative to original one of MB. Fig. 7(b) shows the time dependent ratios of  $C/C_0$ , where  $C_0$  is the original concentration of MB and  $C$  is the concentration of MB irradiated with a 980 nm laser for time  $t$ .  $C$  can be calibrated by comparing the absorption of the MB solution with that of the standard MB solution at a wavelength of 664 nm. Thus, the value of  $C/C_0$  stands for the degradation degree of MB. We can see from Fig. 7(b) that the degradation ratio of MB increases continuously with the irradiation time and reached about 80% after 7 h of irradiation in the presence of  $\text{CaF}_2\text{:Yb@BiVO}_4$  particles. This new type of NIR photocatalyst presented here seems efficient, compared with our previously reported



**Fig. 7.** (a) Absorbance spectra of MB catalyzed by CaF<sub>2</sub>:Yb@BiVO<sub>4</sub> photocatalyst at different irradiation times under 980 nm excitation; (b) the time dependent ratios of  $C/C_0$  in the presence of CaF<sub>2</sub>:Yb, CaF<sub>2</sub>:Yb@BiVO<sub>4</sub> composite and CaF<sub>2</sub>:Yb/BiVO<sub>4</sub> mixture.

NaYF<sub>4</sub>:Yb,Tm@TiO<sub>2</sub> system, since only 65% of degradation ratio was achieved with 14 h of NIR irradiation for the latter [32].

To getting an optimum ratio of CaF<sub>2</sub>:Yb to BiVO<sub>4</sub>, we prepared the CaF<sub>2</sub>:Yb@BiVO<sub>4</sub> composites with different CaF<sub>2</sub>:Yb-to-BiVO<sub>4</sub> molar ratios (10:0.5, 10:1, 10:2, 10:3, 10:4, respectively). The photocatalysis was performed with NIR irradiation for these composites, as shown in Fig. S1 (Supplementary Information). We can see that the most highest photocatalytic activity is obtained for the composite with CaF<sub>2</sub>:Yb-to-BiVO<sub>4</sub> molar ratio of 10:2. Therefore, the composite with CaF<sub>2</sub>:Yb-to-BiVO<sub>4</sub> molar ratio of 10:2 was chosen for the following discussion.

In our previously reported NaYF<sub>4</sub>:Yb,Tm@TiO<sub>2</sub> system, a two-step energy transfer of  $Yb^{3+} \rightarrow Tm^{3+} \rightarrow TiO_2$  was involved to realize NIR photocatalysis so that the ultimate photo quantum yield for exciting TiO<sub>2</sub> might be very low [32]. Another example involving two-step energy transfer for NIR photocatalysis is the photocatalyst BiVO<sub>4</sub>/CaF<sub>2</sub>:Er<sup>3+</sup>,Tm<sup>3+</sup>,Yb<sup>3+</sup>, in which the successive energy transfer from Yb<sup>3+</sup> to Tm<sup>3+</sup> occurs first, and then the excited Tm<sup>3+</sup> transfer its energy to BiVO<sub>4</sub> [53]. In comparison, only a one-step energy transfer of  $Yb^{3+}$ -dimers  $\rightarrow$  BiVO<sub>4</sub> occurs for NIR photocatalysis in our present photocatalytic CaF<sub>2</sub>:Yb@BiVO<sub>4</sub> system. The reduction of energy transfer procedures might be responsible for the improvement of photocatalytic activity.

To demonstrate the origin of MB degradation upon NIR irradiation in the presence of CaF<sub>2</sub>:Yb@BiVO<sub>4</sub> particles, the parallel experiments were performed as follows. (i) To examine whether photolysis of MB occur under NIR irradiation, MB solution was

irradiated with a NIR laser in the absence of CaF<sub>2</sub>:Yb and BiVO<sub>4</sub>. In this case, almost no degradation of MB occurred. (ii) To examine whether thermal degradation of MB occur, MB solution was irradiated with NIR light in the presence of CaF<sub>2</sub>:Yb, and almost no MB degradation was observed. As we know, both NIR irradiation and nonradiative relaxations of excited Yb<sup>3+</sup> ions can generate thermal energy. Therefore, The temperature of MB solution was recorded with time upon 980 nm irradiation in the presence of CaF<sub>2</sub>:Yb. The temperature variation is limited with an increase from 12 °C to 40 °C, which is not enough to cause thermal degradation of MB significantly. The above control experiments indicate that the degradation of MB under NIR irradiation in the presence of CaF<sub>2</sub>:Yb@BiVO<sub>4</sub> is caused mostly by photocatalysis, rather than by photolysis or thermal degradation.

For comparing the difference in the photocatalytic activities for the CaF<sub>2</sub>:Yb@BiVO<sub>4</sub> composite and CaF<sub>2</sub>:Yb/BiVO<sub>4</sub> mixture (the same CaF<sub>2</sub>-to-BiVO<sub>4</sub> molar ratio as that in the composite), MB solution was irradiated by NIR light in the presence of CaF<sub>2</sub>:Yb/BiVO<sub>4</sub> mixture, and 18% of MB was found to be decomposed within 7 h, which is four times lower than the case of CaF<sub>2</sub>:Yb@BiVO<sub>4</sub> composite (~80%). This could be attributed to the difference of their energy migration routes, as has been discussed in the 'Photoluminescence' section. In the CaF<sub>2</sub>:Yb@BiVO<sub>4</sub> composite, CaF<sub>2</sub>:Yb and BiVO<sub>4</sub> particles attach closely to each other and form compact interfaces, which benefits FRET processes. Moreover, the energy transfer rate from excited Yb-dimers to BiVO<sub>4</sub> is larger than the spontaneous radiative transition rate, leading to a high excitation efficiency of BiVO<sub>4</sub> by NIR photons via a FRET process. Therefore, in the CaF<sub>2</sub>:Yb@BiVO<sub>4</sub> composite, a relatively high photon quantum yield can be achieved to activate BiVO<sub>4</sub>, resulting in a relatively high photocatalytic activity. In contrast, there are no contact interfaces between CaF<sub>2</sub>:Yb and BiVO<sub>4</sub> particles in the CaF<sub>2</sub>:Yb/BiVO<sub>4</sub> mixture, and thus BiVO<sub>4</sub> can be excited via a radiation-reabsorption process. The radiation-reabsorption efficiency is low due to a large distance between CaF<sub>2</sub>:Yb and BiVO<sub>4</sub> particles, finally resulting in a low photocatalytic activity. These results indicate that FRET is an important mechanism in the NIR photocatalytic activity.

In addition to high photocatalytic activity, the photochemical stability and reproducibility are also important factors in the practical applications. The stability and durability of CaF<sub>2</sub>:Yb@BiVO<sub>4</sub> composites are assessed by performing recycling experiments, as shown in Fig. 8. No obvious loss in the activity can be observed after five cycles, indicating the CaF<sub>2</sub>:Yb@BiVO<sub>4</sub> composite is stable and not corroded in spite of a long time of NIR irradiation.

#### 4. Conclusions

The powder sample of CaF<sub>2</sub>:1%Yb<sup>3+</sup> was prepared using a high temperature solid-state reaction method, and BiVO<sub>4</sub> nanoparticles were deposited on the surface of CaF<sub>2</sub>:1%Yb<sup>3+</sup> powders by a hydrothermal method. XRD, TEM, EDX, Raman and PL spectral analysis revealed that BiVO<sub>4</sub> nanocrystals were attached around CaF<sub>2</sub>:1%Yb<sup>3+</sup> particles, forming CaF<sub>2</sub>:1%Yb<sup>3+</sup>@BiVO<sub>4</sub> composites. Under excitation of a 980 nm laser, CaF<sub>2</sub>:1%Yb<sup>3+</sup> emits bright green light via cooperative luminescence of Yb<sup>3+</sup>-dimers. In the CaF<sub>2</sub>:1%Yb<sup>3+</sup>@BiVO<sub>4</sub> composite, cooperative energy transfer of a Yb<sup>3+</sup>-dimer to BiVO<sub>4</sub> takes place under NIR excitation, leading to an indirect excitation of BiVO<sub>4</sub> by NIR light via a one-step energy transfer, as indicated by steady-state and dynamic fluorescence spectroscopy. The degradation of MB exposed to CaF<sub>2</sub>:1%Yb<sup>3+</sup>@BiVO<sub>4</sub> composites upon NIR radiation demonstrated the NIR-driven photocatalytic capability. It is noteworthy that our present catalytic system CaF<sub>2</sub>:1%Yb<sup>3+</sup>@BiVO<sub>4</sub> exhibits high photocatalytic activity with a nearly 80% degradation ratio of MB in 7 h of NIR light irradiation, compared with that of our previously

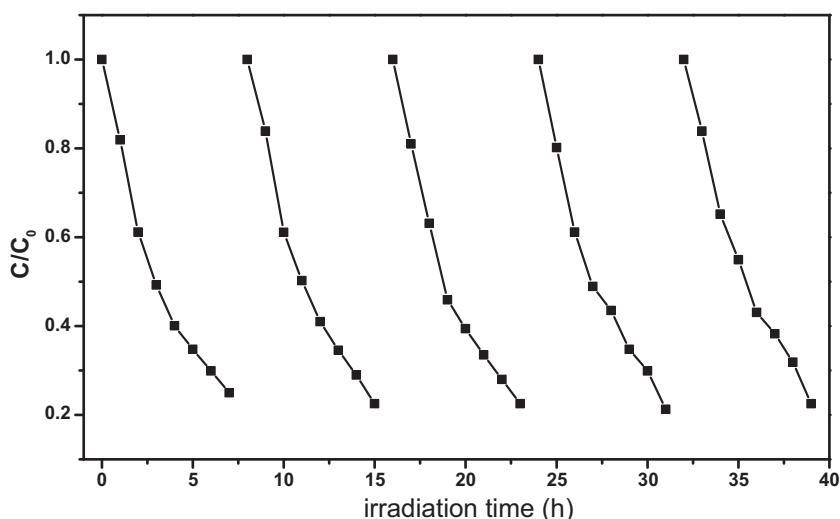


Fig. 8. The time dependent  $C/C_0$  in the presence of  $\text{CaF}_2:\text{Yb@BiVO}_4$  composite under 980 nm excitation during five repeated photocatalytic cycles.

reported systems ( $\text{NaYF}_4:\text{Yb}$ ,  $\text{Tm@TiO}_2$ ), for which ~65% of degradation ratio of MB was obtained within 14 h of NIR irradiation. No obvious loss in the activity can be observed after five photocatalysis cycles, indicating a good photochemical stability.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.12.027>.

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